

Claims

1. A novel heterogeneous catalytic composition comprising a solid support having deposited thereon a catalytically active material which is practically insoluble in variety of liquid media, the said solid material consisting of catalytically active anionic entities with group IIA metal ions.
2. A catalyst as claimed in claim 1 wherein, the catalytic active material is molecularly well defined.
3. A catalyst as claimed in claim 1 wherein, the catalytically active entity is deposited on the external and the pore surfaces of the solid support, pores of which are predominantly of diameter greater than about 20 \AA .
4. A catalyst as claimed in claim 1 wherein, the pores of solid support having a pore diameters ranging from about $3 - 3000 \text{ \AA}$.
5. A catalyst as claimed in claim 1 wherein, the solid support is chemically inactive solid material.
6. A catalyst as claimed in claim 1 wherein, the porous solid support is powder, granules, flakes or pellets of regular or irregular shapes, sheets, monolith, ropes and woven fabric of fibrous solids.
7. A catalyst as claimed in claim 1 wherein, the porous solid support is mechanically robust and thermally stable solid, insoluble in reaction media.
8. A catalyst as claimed in claim 1 wherein, the catalytically active entity is insoluble in reaction media, which are selected from organic, aqueous, flours, non-aqueous ionic liquids and supercritical fluid phases.
9. A catalyst as claimed in claim 1 wherein, the catalytically active solid material is a thermally stable solid material having melting point greater than 100°C .
10. A catalyst as claimed in claim 1 wherein, the catalytically active material is a non-subliming solid.
11. A catalyst as claimed in claim 1 comprising of solid support having deposited thereon catalytically active entity which remains as a stable composite solid in gas, liquid and gas-liquid phases.
12. A catalyst as claimed in claim 11 wherein, the liquid phase is selected from organic, aqueous, flours, non-aqueous ionic liquids and supercritical fluid phases or mixture thereof containing reactants, products and promoters.
13. A catalyst as claimed in claim 1, which remains as a physically stable composite solid in gas or liquid phases over a temperature range of -78 to 300°C .

14. A catalyst as claimed in claim 1, which remains as a physically stable composite solid in gas or liquid phases over pressure ranging from 5 to 5000 psi.

15. A catalyst as claimed in claim 1 wherein, group IIA metal used is a cation having +2 charge.

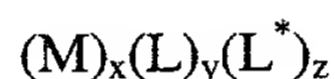
5 16. A catalyst as claimed in claim 1 wherein, group IIA metal used is selected from calcium, strontium, barium and mixtures thereof.

17. A catalyst as claimed in claim 1 wherein, group IIA metal used is selected independently or in combination with other group IIA metals.

10 18. A catalyst as claimed in claim 1 wherein, catalytically active entity is an anion having two or more negative charges.

19. A catalyst as claimed in claim 1 wherein, the catalytically active entity is independently selected from metal complexes, quaternary compounds, metaloxoanions, polyoxometallates and combinations thereof.

15 20. A catalyst as claimed in claim 19 wherein, the metal complexes having a general formula



20 wherein M is catalytic metal atom or ion of a coordination complex is a transition metal from group IIIB, IVB, VB, VIB, VIIB, IB or IIB of the periodic table of elements and is selected independently, x is ranging from 1 to 60, L is selected from aliphatic, aromatic and heterocyclic compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from $-SO_3^-$, $-SO_2^-$, $-PO_3^{2-}$, $-COO^-$, $-O^-$, AsO_3^{2-} and $-S^-$, y is at least 1, L^* is a radical selected from

25 organic anion, inorganic anion and coordinating compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene, $=C:$ having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl and Z is ranging from 0 to 7.

30 21. A catalyst as claimed in claim 19 wherein, the quaternary compound is having a general formula



wherein, $I = 4$ for $Y^+ = N^+, P^+, As^+$; $I = 3$ for $Y^+ = S^+$ and R^* is selected independently from alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl

bearing at least one or more negatively charged functional groups independently selected from $-\text{SO}_3^-$, $-\text{SO}_2^-$, $-\text{PO}_3^{2-}$, $-\text{COO}^-$, $-\text{O}^-$, AsO_3^{2-} and $-\text{S}^-$ and Z is an anion selected from organic anion, inorganic anion and coordination complex anion.

5 22. A catalyst as claimed in claim 1 wherein, the insoluble catalytically active material optionally comprising catalytically inert additive.

23. A catalyst as claimed in claim 22 wherein, the catalytically inert additive is an anion having two or more negative charges.

10 24. A catalyst as claimed in claim 22 wherein, the catalytically inert additive is an anion, which is independently selected from organic, inorganic anions or in combination thereof.

15 25. A catalyst as claimed in claim 22 wherein, the catalytically inert additive is selected from ligand compounds wherein, ligand compounds contain at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alcoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from $-\text{SO}_3^-$, $-\text{SO}_2^-$, $-\text{PO}_3^{2-}$, $-\text{COO}^-$, $-\text{O}^-$, AsO_3^{2-} and $-\text{S}^-$.

26. A catalyst as claimed in claim 1 wherein, the amount of catalytically active entity employed is 40 % weight or less.

20 27. A catalyst as claimed in claim 1 wherein the amount of catalytically inert additive employed is in the proportion of 0 to 200-weight % of catalytically active entity.

28. A catalyst as claimed in claim 1 which, can be employed to catalyze reactions in gas phase or in slurry phase.

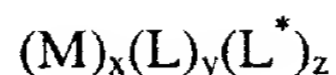
25 29. A catalyst as claimed in claim 1 further comprising a film of high boiling liquid deposited on the solid catalyst.

30 30. A novel heterogeneous catalytic composition comprising a solid support having deposited thereon a catalytically active material which is practically insoluble in variety of liquid media, the said solid material consisting of catalytically active anionic entities and catalytically inactive anionic additive with group IIA metal ions.

31. A catalyst as claimed in claim 30 wherein, the catalytic active material is molecularly well defined.

32. A catalyst as claimed in claim 30 wherein, the catalytically active entity is deposited on the external and the pore surfaces of the solid support, pores of which are predominantly of diameter greater than about 20 \AA .
33. A catalyst as claimed in claim 30 wherein, the pores of solid support having a pore diameters ranging from about $3 - 3000 \text{ \AA}$.
34. A catalyst as claimed in claim 30 wherein, the solid support is chemically inactive solid material.
35. A catalyst as claimed in claim 30 wherein, the porous solid support is powder, granules, flakes or pellets of regular or irregular shapes, sheets, monolith, ropes and woven fabric of fibrous solids.
36. A catalyst as claimed in claim 30 wherein, the porous solid support is mechanically robust and thermally stable solid, insoluble in reaction media.
37. A catalyst as claimed in claim 30 wherein, the catalytically active entity is insoluble in reaction media, which are selected from organic, aqueous, flours, non-aqueous ionic liquids and supercritical fluid phases.
38. A catalyst as claimed in claim 30 wherein, the catalytically active solid material is a thermally stable solid material having melting point greater than 100°C .
39. A catalyst as claimed in claim 30 wherein, the catalytically active material is a non-subliming solid.
40. A catalyst as claimed in claim 30 comprising of solid support having deposited thereon catalytically active entity which remains as a stable composite solid in gas, liquid and gas-liquid phases.
41. A catalyst as claimed in claim 40 wherein, the liquid phase is selected from organic, aqueous, flours, non-aqueous ionic liquids and supercritical fluid phases or mixture thereof containing reactants, products and promoters.
42. A catalyst as claimed in claim 30, which remains as a physically stable composite solid in gas or liquid phases over a temperature range of -78 to 300°C .
43. A catalyst as claimed in claim 30, which remains as a physically stable composite solid in gas or liquid phases over pressure ranging from 5 to 5000 psi.

44. A catalyst as claimed in claim 30 wherein, group IIA metal used is a cation having +2 charge.
45. A catalyst as claimed in claim 30 wherein, group IIA metal used is selected from calcium, strontium, barium and mixtures thereof.
- 5 46. A catalyst as claimed in claim 30 wherein, group IIA metal used is selected independently or in combination with other group IIA metals.
47. A catalyst as claimed in claim 30 wherein, catalytically active entity is an anion having two or more negative charges.
48. A catalyst as claimed in claim 30 wherein, catalytically active entity is
10 independently selected from metal complexes, quaternary compounds, metaloxoanions, polyoxometallates and combinations thereof.
49. A catalyst as claimed in claim 30 wherein, the amount of catalytically active entity employed is 40 % weight or less.
50. A catalyst as claimed in claim 30 wherein the amount of catalytically inert additive
15 employed is 0 to 200-weight % of catalytically active entity.
51. A catalyst as claimed in claim 30 which, can be employed to catalyze reactions in gas phase or in slurry phase.
52. A catalyst as claimed in claim 30 comprising a film of high boiling liquid deposited on the solid catalyst.
- 20 53. A process for preparing a catalytically active material, said process comprising interacting a solution consisting of a catalytically inactive additive and a catalytically active entity with a solution of group IIA metal cation and obtaining a precipitate, wherein catalytically inactive additive is independently selected from
25 anions having at least two or more negative charges, ligand compounds containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alcoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from
30 $-\text{SO}_3^-$, $-\text{SO}_2^-$, $-\text{PO}_3^{2-}$, $-\text{COO}^-$, $-\text{O}^-$, AsO_3^{2-} and $-\text{S}^-$, and combination thereof; the catalytically active entity is independently selected from metal complexes, quaternary compounds, metal oxo anions, polyoxometallates and combinations thereof, the metal complexes is having a general formula



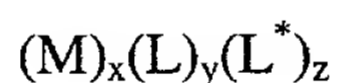
wherein M is catalytic metal atom or ion of a coordination complex is a transition metal from group IIIB, IVB, VB, VIB, VIIB, IB or IIB of the periodic table of elements, x is ranging from 1 to 60, L is selected from aliphatic, aromatic and heterocyclic compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from $-\text{SO}_3^-$, $-\text{SO}_2^-$, $-\text{PO}_3^{2-}$, $-\text{COO}^-$, $-\text{O}^-$, AsO_3^{2-} and $-\text{S}^-$, y is at least 1, L^* is radical selected from organic anion, inorganic anion and coordinating compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene, $=\text{C}$: having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl, z is ranging from 0 to 7 and the quaternary ammonium compound has a general formula



wherein, $I = 4$ for $Y^+ = \text{N}^+$, P^+ , As^+ ; $I = 3$ for $Y^+ = \text{S}^+$ and R^* is selected independently from alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from $-\text{SO}_3^-$, $-\text{SO}_2^-$, $-\text{PO}_3^{2-}$, $-\text{COO}^-$, $-\text{O}^-$, AsO_3^{2-} and $-\text{S}^-$ and Z is anion selected from organic anion, inorganic anion or coordination complex anion; and the group II A metal cation is selected from compounds of Ca^+ , Sr^+ and Ba^+ .

54. A process as claimed in claim 53 wherein, the reaction is carried out in the temperature ranging from -70 to 200°C preferably between -5 to 100°C .
55. A process as claimed in claim 53 wherein, the amount of catalytically active entity employed is 40 % weight or less.
56. A process as claimed in claim 53 wherein, the amount of catalytically inert additive employed is in the proportion of 0 to 200-weight % of catalytically active entity.
57. A process as claimed in claim 53 wherein, the catalyst can be employed to catalyze reactions in gas phase or in slurry phase.
58. A process as claimed in claim 53 wherein, a film of high boiling liquid is preferably deposited on the solid catalyst.

59. A process for the preparation of a heterogeneous catalytic formulation as a solid composite comprising of porous solid support having deposited thereon a catalytically active solid, said process comprising suspending insoluble solid support in a liquid phase to which a solution of a catalytically inert additive and a catalytically active entity and a solution of group IIA metal cation are added simultaneously with vigorous agitation and allowed to age for 1 to 48 hours wherein, the support is mechanically robust and thermally stable solid in reaction media, having a mean pore diameter in the range of about 3-3000 Å⁰ and existing as powder, granules, flakes or pellets of regular or irregular shapes, sheets, monolith, ropes and woven fabric of fibrous solids and the catalytically inactive additive is independently selected from anions having at least two or more negative charges selected from organic, inorganic, or a compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from -SO₃⁻, -SO₂⁻, -PO₃²⁻, -COO⁻, -O⁻, AsO₃²⁻ and -S⁻, the catalytically active entity is independently selected from metal complexes, quaternary compounds, metaloxoanions, polyoxometallates and combinations, the metal complexes having a general formula



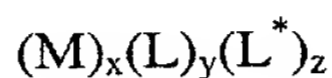
wherein M is catalytic metal atom or ion of a coordination complex is a transition metal from group IIIB, IVB, VB, VIB, VIIB, IB or IIB of the periodic table of elements, x is ranging from 1 to 60, L is selected from aliphatic, aromatic and heterocyclic compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from -SO₃⁻, -SO₂⁻, -PO₃²⁻, -COO⁻, -O⁻, AsO₃²⁻ and -S⁻, y is at least 1, L^{*} is a radical selected from organic anion, inorganic anion and coordinating compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene, =C: having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl, z is ranging from 0 to 7, and the quaternary ammonium compound has a general formula



wherein, $I = 4$ for $Y^+ = N^+, P^+, As^+$; $I = 3$ for $Y^+ = S^+$ and R^* is selected independently from alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from the group consisting of $-SO_3^-, -SO_2^-, -PO_3^{2-}, -COO^-, -O^-, AsO_3^{2-}$ and $-S^-$ and Z is an anion selected from organic anion, inorganic anion and coordination complex anion and the group IIA metal cation is selected from compounds of Ca^{2+} , Sr^{2+} and Ba^{2+} .

60. A process as claimed in claim 59 wherein, the reaction is carried out in the temperature ranging from -70 to $200^\circ C$ preferably between -5 to $100^\circ C$.
61. A process as claimed in claim 59 wherein, the solvent used is selected form aqueous, water miscible organic and mixture thereof.
62. A process as claimed in claim 59 wherein, the solution of catalytically inert additive and catalytically active entity and a solution of group IIA metal cation are added simultaneously over a period of 10 to 1500 min.
63. A process as claimed in claim 59 wherein, the catalyst is recovered by centrifugation, decantation, gravity settling or other techniques of solid liquid separation and solids dried subsequently in vacuum.
64. A process for the preparation of a heterogeneous catalytic formulation as a solid composite comprising of porous solid support having deposited thereon a catalytically active solid, said process comprising impregnating the solid support with the catalytically active entity and the catalytically inert additive followed by drying, dried support having deposited thereon catalytically active entity and the catalytically inert additive is added to a solution of group IIA metal compound, with simultaneous agitation and the suspension is aged for 1 to 48 hours with agitation, wherein the support is mechanically robust and thermally stable solid in reaction media, having a mean pore diameter in the range of about $3-3000 \text{ \AA}^0$ and existing as powder, granules, flakes or pallets of regular or irregular shapes, sheets, monolith, ropes and woven fabric of fibrous solids and catalytically inactive additive is independently selected from anions having at least two or more negative

65. charges which may be organic, inorganic, or a compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from -SO₃⁻, -SO₂⁻, -PO₃²⁻, -COO⁻, -O⁻, AsO₃²⁻ and -S⁻; the catalytically active entity is independently selected from metal complexes, quaternary compounds, metal oxo anions and polyoxometallates or combinations thereof, the metal complexes having a general formula



wherein M is catalytic metal atom or ion of coordination complex is a transition metal from group IIIB, IVB, VB, VIB, VIIB, IB or IIB of the periodic table of elements x is from 1 to 60, L is aliphatic, aromatic and heterocyclic compounds containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from -SO₃⁻, -SO₂⁻, -PO₃²⁻, -COO⁻, -O⁻, AsO₃²⁻ and -S⁻, y is at least 1, L* is a radical selected from organic anion, inorganic anion and coordinating compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene, =C: having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl, z is from 0 to 7 and the quaternary ammonium compound has a general formula



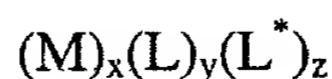
wherein, I = 4 for Y⁺ = N⁺, P⁺, As⁺; I = 3 for Y⁺ = S⁺ and R* is selected independently from alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from -SO₃⁻, -SO₂⁻, -PO₃²⁻, -COO⁻, -O⁻, AsO₃²⁻ and -S⁻ and Z is anion selected from organic anion, inorganic anion or coordination complex anion, and the group IIA metal cation are selected from compounds of Ca²⁺, Sr²⁺ and Ba²⁺.

66. A process as claimed in claim 64 is carried out in the temperature ranging from -70 to 200°C preferably between -5 to 100°C.
67. A process as claimed in claim 64 wherein, the solvent is aqueous, water miscible organic or mixture thereof.

68. A process as claimed in claim 64 wherein, the support having deposited thereon catalytically active entity and catalytically inert additive is added to a solution of group IIA metal compound, with simultaneous agitation over a period of 10 to 1500 min.

69. A process as claimed in claim 64 wherein, the catalyst is recovered by centrifugation, decantation, gravity settling or other techniques of solid liquid separation and solids dried subsequently in vacuum.

70. A process for the preparation of a heterogeneous catalytic formulation as a solid composite comprising of porous solid support having deposited thereon a catalytically active solid, said process is characterized by impregnation of support with a solution of a catalytically inactive additive and a catalytically active entity followed by drying and suspending the solid support having deposited thereon the catalytically inactive additive and the catalytically active entity in water immiscible solvent to which a solution of group IIA metal compound solution is added with vigorous agitation and concurrent removal of low boiling or azeotropic fraction of solvent and the suspension is allowed to age for 1 to 48 hours, wherein the support is mechanically robust and thermally stable solid in reaction media, having a mean pore diameter in the range of about 70-3000 Å and existing as powder, granules, flakes or pellets of regular or irregular shapes, sheets, monolith, ropes and woven fabric of fibrous solids and the catalytically inactive additive is independently selected from anions having at least two or more negative charges which may be organic, inorganic, or a compound containing at least one radical form O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alcoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from $-\text{SO}_3^-$, $-\text{SO}_2^-$, $-\text{PO}_3^{2-}$, $-\text{COO}^-$, $-\text{O}^-$, AsO_3^{2-} and $-\text{S}^-$; the catalytically active entity is independently selected from metal complexes, quaternary compounds, metal oxo anions and polyoxometallates or combinations thereof, the metal complexes having a general formula



wherein M is catalytic metal atom or ion of coordination complex is a transition

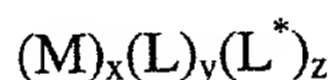
metal from group IIIB, IVB, VB, VIB, VIIB, IB or IIB of the periodic table of elements, x is from 1 to 60, L is aliphatic, aromatic and heterocyclic compounds containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from $-\text{SO}_3^-$, $-\text{SO}_2^-$, $-\text{PO}_3^{2-}$, $-\text{COO}^-$, $-\text{O}^-$, AsO_3^{2-} and $-\text{S}^-$, y is at least 1, L^* is radical selected from organic anion, inorganic anion and coordinating compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene, $=\text{C}:$ having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl, z is from 0 to 7, and quaternary ammonium compound has a general formula



wherein, $I = 4$ for $\text{Y}^+ = \text{N}^+, \text{P}^+, \text{As}^+$; $I = 3$ for $\text{Y}^+ = \text{S}^+$ and R^* is selected independently from alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from $-\text{SO}_3^-$, $-\text{SO}_2^-$, $-\text{PO}_3^{2-}$, $-\text{COO}^-$, $-\text{O}^-$, AsO_3^{2-} and $-\text{S}^-$ and Z is anion selected from organic anion, inorganic anion or coordination complex anion, the group IIA metal cation are selected from compounds of Ca^{2+} , Sr^{2+} and Ba^{2+} .

71. A process as claimed in claim 69 is carried out in the temperature ranging from -70 to 200°C .
72. A process as claimed in claim 69 wherein, the solvent employed to form a solution of group IIA metal ion is aqueous, water miscible organic or mixture thereof.
73. A process as claimed in claim 69 wherein, the solvent employed is water immiscible organic solvent, having boiling point in the range 40 to 200°C .
74. A process according to claim 69 wherein, the catalyst is recovered by centrifugation, decantation or gravity settling or other techniques of solid liquid separation and solids dried subsequently in vacuum.
75. A process for the preparation of a heterogeneous catalytic formulation as a solid composite comprising of porous solid support having deposited thereon a group IIA

metal compound followed by drying and suspending the solid support having deposited thereon group IIA metal in water immiscible solvent to which a solution of catalytically active entity and catalytically inactive additive is added with vigorous agitation and concurrent removal of low boiling or azeotropic fraction of solvent and the suspension is allowed to age for 1 to 48 hours, wherein the support is mechanically robust and thermally stable solid in reaction media, having a mean pore diameter in the range of about 3-3000 Å⁰ and existing as powder, granules, flakes or pellets of regular or irregular shapes, sheets, monolith, ropes and woven fabric of fibrous solids and the catalytically inactive additive is independently selected from anions having at least two or more negative charges which may be organic, inorganic, or a compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from -SO₃⁻, -SO₂⁻, -PO₃²⁻, -COO⁻, -O⁻, AsO₃²⁻ and -S⁻¹; the catalytically active entity is independently selected from metal complexes, quaternary compounds, metal oxo anions and polyoxometallates or combinations thereof, the metal complexes having a general formula



wherein M is catalytic metal atom or ion of coordination complex is a transition metal from group IIIB, IVB, VB, VIB, VIIB, IB or IIB of the periodic table of elements, x is from 1 to 60, L is aliphatic, aromatic and heterocyclic compounds containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from -SO₃⁻, -SO₂⁻, -PO₃²⁻, -COO⁻, -O⁻, AsO₃²⁻ and -S⁻, y is at least 1, L* is a radical selected from organic anion, inorganic anion and coordinating compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene, =C: having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl, z is from 0 to 7, and the quaternary ammonium compound has a general formula



wherein, $I = 4$ for $Y^+ = N^+, P^+, As^+$ $I = 3$ for $Y^+ = S^+$ and R^* is selected independently from alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from $-SO_3^-$, $-SO_2^-$, $-PO_3^{2-}$, $-COO^-$, $-O^-$, AsO_3^{2-} and $-S^-$ and Z is anion selected from organic anion, inorganic anion or coordination complex anion and the group IIA metal cation are selected from compounds of Ca^{+2} , Sr^{+2} and Ba^{+2} .

76. A process as claimed in claim 74 is carried out in the temperature ranging from -70 to $200^\circ C$.

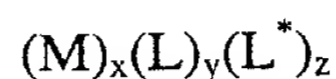
77. A process as claimed in claim 74 wherein, the solvent employed to form a solution of group IIA metal ion is aqueous, water miscible organic or mixture thereof.

78. A process as claimed in claim 74 wherein, the solvent employed is water immiscible organic solvent, having boiling point in the range 40 to $200^\circ C$.

79. A process as claimed in claim 74 wherein, the catalyst is recovered by centrifugation, decantation, gravity settling or other techniques of solid liquid separation and solids dried subsequently in vacuum.

80. A process for the preparation of a heterogeneous catalytic formulation as a solid composite comprising fluidizing solid support in the current of gasses and spraying a solution of catalytically active entity and a catalytically inert additive in such a way that the catalytically active entity and the catalytically inert additive are deposited on the solid support, the fluidization of solid is continued for 1 to 48 hours and a solution of group IIA metal compound is subsequently sprayed and fluidization of solid is further continued for 1 to 48 hours and solids are recovered, wherein, the support is mechanically robust and thermally stable solid in reaction media, having a mean pore diameter in the range of about 70-3000 \AA and existing as powder, granules, flakes or pellets of regular or irregular shapes, sheets, monolith, ropes and woven fabric of fibrous solids and the catalytically inactive additive is independently selected from anions having at least two or more negative charges which may be organic, inorganic, or a compound containing at least one radical form O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from

-SO₃⁻, -SO₂⁻, -PO₃²⁻, -COO⁻, -O⁻, AsO₃²⁻ and -S⁻; the catalytically active entity is independently selected from metal complexes, quaternary compounds, metal oxo anions and polyoxometallates or combinations thereof, the metal complexes having a general formula



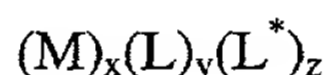
wherein M is catalytic metal atom or ion of coordination complex is a transition metal from group IIIB, IVB, VB, VIB, VIIB, IB or IIB of the periodic table of elements, x is from 1 to 60, L is aliphatic, aromatic and heterocyclic compounds containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from -SO₃⁻, -SO₂⁻, -PO₃²⁻, -COO⁻, -O⁻, AsO₃²⁻ and -S, y is at least 1, L* is a radical selected from organic anion, inorganic anion and coordinating compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene, =C: having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl, z is from 0 to 7, and quaternary ammonium compound has a general formula



wherein, I = 4 for Y⁺ = N⁺, P⁺, As⁺; I = 3 for Y⁺ = S⁺ and R* is selected independently from alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from -SO₃⁻, -SO₂⁻, -PO₃²⁻, -COO⁻, -O⁻, AsO₃²⁻ and -S⁻ and Z is anion selected from organic anion, inorganic anion or coordination complex anion, the group IIA metal cation are selected from compounds of Ca⁺², Sr⁺² and Ba⁺².

81. A process as claimed in claim 79 is carried out in the temperature ranging from -70 to 200°C.
82. A process as claimed in claim 79 wherein, the solvent employed to form a solution of group IIA metal ion is aqueous, water miscible organic or mixture thereof.
83. A process for the preparation of a heterogeneous catalytic formulation as a solid composite comprising of tumbling solid support in the rotating pan under current of gasses, a solution of catalytically active entity and a catalytically inert additive is

sprayed in such a way that the catalytically active entity and the catalytically inert additive are deposited on the solid support, the tumbling of solid is continued for 1 to 48 hours and a solution of group IIA metal compound is subsequently sprayed and tumbling of solid is further continued for 1 to 48 hours and solids are recovered, wherein the support is mechanically robust and thermally stable solid in reaction media, having a mean pore diameter in the range of about 70-3000 Å⁰ and existing as powder, granules, flakes or pellets of regular or irregular shapes, sheets, monolith, ropes and woven fabric of fibrous solids and the catalytically inactive additive is independently selected from anions having at least two or more negative charges which may be organic, inorganic, or a compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from -SO₃⁻, -SO₂⁻, -PO₃²⁻, -COO⁻, -O⁻, AsO₃²⁻ and -S⁻; the catalytically active entity is independently selected from metal complexes, quaternary compounds, metal oxo anions and polyoxometallates or combinations thereof, the metal complexes having a general formula



wherein M is catalytic metal atom or ion of coordination complex is a transition metal from group IIIB, IVB, VB, VIB, VIIB, IB or IIB of the periodic table of elements, x is from 1 to 60, L is aliphatic, aromatic and heterocyclic compounds containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from -SO₃⁻, -SO₂⁻, -PO₃²⁻, -COO⁻, -O⁻, AsO₃²⁻ and -S⁻ y is at least 1, L^{*} is a radical selected from organic anion, inorganic anion and coordinating compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene, =C: having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl, z is from 0 to 7 and the quaternary ammonium compound has a general formula



wherein, I = 4 for Y⁺ = N⁺, P⁺, As⁺; I = 3 for Y⁺ = S⁺ and R^{*} is selected independently from alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently

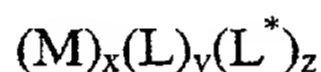
selected from $-\text{SO}_3^-$, $-\text{SO}_2^-$, $-\text{PO}_3^{2-}$, $-\text{COO}^-$, $-\text{O}^-$, AsO_3^{2-} and $-\text{S}^-$ and Z is anion selected from organic anion, inorganic anion or coordination complex anion and the group IIA metal cation are selected from compounds of Ca^{+2} , Sr^{+2} and Ba^{+2} .

84. A process as claimed in claim 82 is carried out in the temperature ranging from -70 to 200°C .

85. A process as claimed in claim 82 wherein, the solvent employed to form solutions is aqueous, water miscible organic or mixture thereof.

86. A process as claimed in claim 82 wherein, the solutions are sprayed simultaneously or sequentially.

87. Use of a catalyst as claimed in claim 1 in a reaction wherein, the reaction is selected from analogous reactions that are catalyzed by catalytically active entity in liquid phase, the catalytically active entity is independently selected from metal complexes, quaternary compounds, metal oxo anions and polyoxometallates or combinations thereof such that metal complexes having a general formula



wherein M is catalytic metal atom or ion of coordination complex is a transition metal from group IIIB, IVB, VB, VIB, VIIB, IB or IIB of the periodic table of elements, x is from 1 to 60, L is aliphatic, aromatic and heterocyclic compounds containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl y is at least 1, L^* is a radical selected from organic anion, inorganic anion and coordinating compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene, $=\text{C}$: having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl, z is from 0 to 7, and the quaternary ammonium compound has a general formula



wherein, $I = 4$ for $\text{Y}^+ = \text{N}^+$, P^+ , As^+ ; $I = 3$ for $\text{Y}^+ = \text{S}^+$ and R^* is selected independently from alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl and Z is anion selected from organic anion, inorganic anion or coordination complex anion.